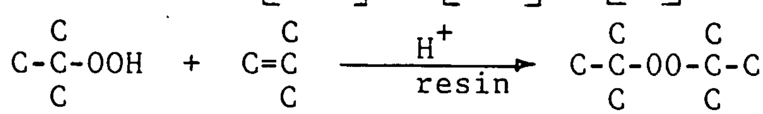
of the extracting ability of the large amount of isobutane. Especially low in concentration should be the t-butanol and hydroperoxide. Direct combustion of this stream as a composite with other streams containing more combustibles would be the anticipated mode of disposal.

Alkylation Of t-Butyl Hydroperoxide With Isobutylene

The alkylation of t-butyl hydroperoxide with isobutylene either pure or contained in a mixed butene stream is a very facile reaction which is acid catalyzed. Most of our work has been conducted with pure isobutene, with a limited amount of work done with normal butenes alone to establish that a nil amount of alkylation is occurring. Alkylation is effected by strong acid ion exchange resin of the sulfonic acid type preferably with the macro recticular structure that is most beneficial for organic reactions. Other solid acids are also effective and do not require the removal of the organics by distillation which is our preferred operating conditions. The reaction appears to be first order with respect to isobutylene, t-butyl hydroperoxide and acid.

$$r = k \left[iC_4^=\right] \cdot \left[tBHP\right] \cdot \left[H^+\right]$$



Our alkylation is based on the following design case shown in Table 3.

Table 3
Alkylation Of t-Butyl Hydroperoxide
Design Case

Temperature	60^oC
Pressure	200 psig
Catalyst	H^+ resin

tBHP:$iC_4^=$: tBA (molar)	1.0:1.23:.49
WHSV	2.0 hr^{-1}
Conversion M%	
t-butyl hydroperoxide	100
isobutylene	81
Selectivity mol%	
di-t-butyl peroxide	100

t-Butyl hydroperoxide alkylation with isobutylene shows a reaction rate constant 10 to 20 times greater than the rate constant of alkylation of either water or methanol. As a consequence of this high rate constant, the avoidance of self alkylation to disiobutylene and more complete utilization of the contained isobutylene are possible in this system than in the alkylation of methanol. Ideal comparative systems for design or optimization consideration are the MtBE systems from isobutylene and tBA. The literature is replete with studies of various economic and technical optimizations. DtBP production has strong rate and equilibrium advantages.

Alkylation of tBHP has also been studied using mixed butene streams and tBA. Both are realistic potential candidates for the facile production of DtBP where the economics and markets exist for the production of gasoline octane enhancers of either the tBA alcohol type or the MtBE ether type. Our choice for this design is predicated on the basis of minimizing co-production. The alkylation block therefore functions as an internal process service and provides no economic upgrade although it does possess this capacity.

Played for economics only this section would be operated with a mixed butenes refinery stream to provide a dual upgrade of eventually acetone and/or tBA from the isobutene and an upgraded purified n-butene-1 stream for copolymerization with ethylene.

The design of Block 2 is based on the kinetics of the reaction which suggests that a plug flow reactor be used to attain the highest possible level of conversion of both the t-butyl hydroperoxide and isobutylene. We chose as the terminal point of the reaction a quantitative conversion of the t-butyl hydroperoxide and 81% conversion of the contained isobutylene. Much higher productivity is easily obtained from this section.

There are a number of approaches for the design of this alkylator. We have chosen a tube in shell configuration fabricated of 304 S.S. The tubes are filled with ion exchange resin and the reactants flow upward through the tubes while cooling water flows concurrently outside the tubes. This scheme provides maximum cooling during the earliest part of the reaction which evolves the most heat of reaction. DtBP is a more stable entity than tBHP to temperature and most every other catalyst including acids. For this reason we would prefer maximum reaction to occur at milder conditions than 60°C where the kinetics are favorable. The final portions of the reaction, we seek to push to completion, is then conducted at a somewhat higher temperature, where the reaction rate constant is greater, but the possibility of loss of active components is minimized.

Alternative approaches for this design are use of a packed bed reactor with multiple withdrawal and injection points to provide cooling and the use of a back mixed reactor cooled by normal means where a high percentage of the reaction is compeleted, followed by an adiabatic tubular plug flow reactor. In any of these systems the effluent should be monitored for strong acid and neutralized by weak salts if any is present. Data in Table 4 is used in the design of Block 2.

Table 4

Alkylation - Physical Properties

Heat Of Reaction

$tBHP + iC_4^= \longrightarrow DtBP$ H = -22,100 BTU/mol/lb.

Heats Of Vaporization

n-butene	C_4H_8	MW 56	11,400 BTU/mol/lb.
isobutylene	C_4H_8	MW 56	10,427 BTU/mol/lb.
t-butanol	$C_4H_{10}O$	MW 74	18,910 BTU/mol/lb.
acetone	C_3H_6O	MW 58	13,877 BTU/mol/lb.

Vapor Pressure

$$\text{Log}_{10}\ P = (-.2185\ A/K) + B$$

K = ° Kelvin
P = mm Hg

	A	B
n-butene	622.6	7.882542
isobutylene	5742.9	7.601563
t-butanol	10413.2	9.193472
acetone	7641.5	7.904024

Heat Capacities

n-butene	.94 BTU/lb/°C
isobutylene	.939BTU/lb/°C
t-butanol	1.31 BTU/lb/°C
acetone	.946BTU/lb/°C

At this point in time we do not envision a need to purify the DtBP by distillation. This is possible if the need for it should be established. A particularly efficacious way is by azeotropic distillation with methanol.

Engineering Safety and Environmental

It is believed that t-butyl hydroperoxide is the highest peroxy homologue that possesses sufficient energy density (peroxy oxygen/weight) to detonate in the absence of oxygen. Di-t-butyl peroxide has a considerably lower energy density than does the hydroperoxide and accordingly is viewed as being quite a stable peroxide. The stability of any peroxide however should not be taken lightly because under proper conditions an adiabatic temperature rise can promote a very rapid decomposition to volatile products which can generate very high pressures with the potential to rupture reaction vessels. The safety concerns while less with DtBP must make provisions for the unexpected. The ability to quench when a certain threshold temperature is reached must be provided for in the design. A reservoir of tBA of suitable quantity to act both as a diluent source and as a dump would probably be the best means of controlling a runaway reaction. This reservoir could be common to both safety considerations in peroxidation and alkylation.

Environmental concerns arising from Block 2 are non-existant to the extent that no streams leave the confines of the plant and move into the environment for disposal.

Block 2 tBHP Alkylation

Process Description

T-butyl-hydroperoxide (tBHP) is alkylated with isobutylene to DtBP in the liquid phase in the presence of strong acid ion exchange resin. Low temperature (70°C) helps ensure resin stability while maintaining rates (30 min. res. time). Excess isobutylene (23%) ensures complete tBHP conversion in the plug flow reactor.

Excess isobutylene is removed in a single distillation step. Low base temperature of 115°C prevents DtBP decomposition. Product DtBP is immediately cooled and stored for feed to the Redox reactor.

Sizing-Influence of Redox Reaction

Size of Block 1 and 2 are dependent on DtBP utilization in the Redox reaction for the production of glycols.

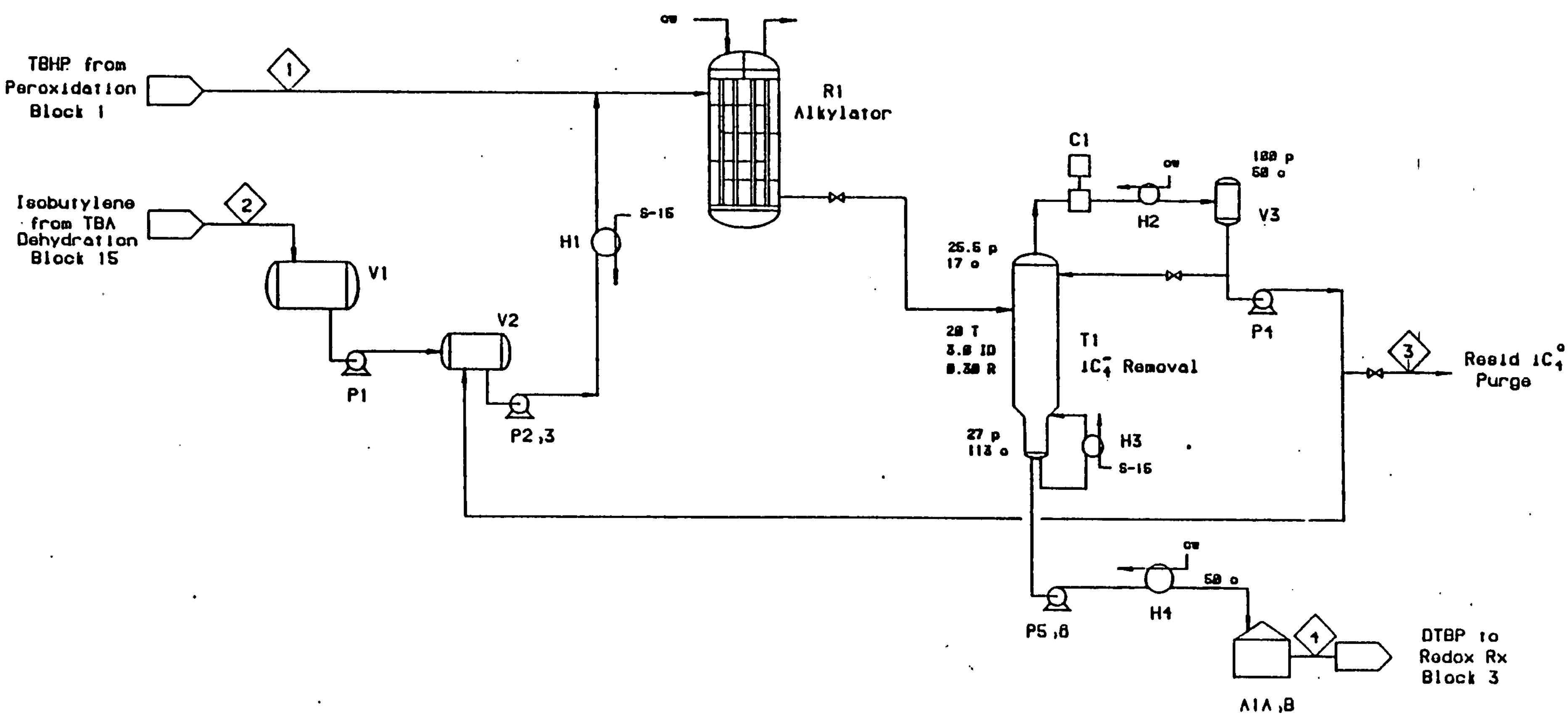
This case - tBHP utilization = 2.72 wt. ratio.

Range - tBHP utilization = 2.1 - 3.64 wt. ratio.

Utilities

		Units/lb. EG
Electricity	KWH	.0015
Steam lb.	S-15	.06
Cooling Water	gal.	.8

FIGURE B-1
BLOCK 2 -- TBHP ALKYLATION
Detailed Process Flow Diagram



Block 2 Alkylation

Equipment Type	Delivered Equipment Cost M$	BL/DEC Ratio	Battery Limits Cost M$
Vessels	135.9	5.09	691.9
Atm. Tanks	157.2	2.55	400.9
Towers	39.2	5.89	230.9
Xchangers	699.5	1.91	1,336.0
Pumps	22.1	10.75	238.7
Compressors	48.4	3.46	167.4
Total	1,102.4	2.78	3,065.8

MATERIAL FLOWS

Alkylation - 200

	From 800	From 100	To 300	iC_4 Purge
$iC_4^=$	280.17			
iC_4		.25	.04	.21
nC_4		.41	.19	.22
H_2O	19.35	21.55	40.90	
tBHP		280.16		
tBA	42.60	137.90	180.54	
DMK		8.55	8.55	.01
MeOH	29.17	8.54	37.71	
EtOH	33.86		33.86	
DtBP			280.16	

Alkylation Block 200

Vessels

	gallons	Matrl.	Press. psia
V0201 $iC_4^=$ Feed	37,500	CS	150
V0202 $iC_4^=$ Surge	4,836	304 SS	175
V0203 T1 OH Receiver	892	304 SS	130

Towers

	Matrl.	Height x Dia.	Press.psig	Trays
T0201 $iC_4^=$ Removal	304 SS	35' x 3'	130	20 304 SS

Atm. Tanks

	Gallons	Matrl.	Roof
A020 1B DtBP Rundown	111,000	Al.	Fixed
A020 1A DtBP Rundown	111,000	Al.	Fixed

Heat Exchangers

	Area Sq.ft.	Type	Design	Matrl. SS/TS	Press psia SS/TS	Design °F
H0201 $iC_4^=$ Preheat	50	S&T	Std.	CS/304	50/200	250
H0202 T1 OH Cond.	446	S&T	Std.	304/304	130/50	150
H0203 T1 Reboil.	297	S&T	Thermo	CS/304	50/50	250
H0204 DtBP Cooler	893	S&T	Std.	304/304	50/50	240
R0201 Alkylator	13,392	S&T	Std.	304/304	200/50	160

Alkylation Block 200

Pumps

	Units	HP	Type	Matrl.		Units	HP	Type	Matrl.
P0201	2	2.7	C	CS	P0204	2	1.9	C	316 SS
P0202	2	4.8	C	316 SS	P0205	2	4.2	C	316 SS
P0203	1	4.8	C	316 SS	P0206	1	4.2	C	316 SS

Compressor

	HP	Type	Matrl.	Driver
C0201 T10H Booster	83	Recip.	CS	Elect. Motor